A HYDROMETALLURGICAL SEPARATION PROCESS OF STEEL MILL ELECTRIC ARC FURNACE (EAF) DUST AND THE PIGMENTS OBTAINED BY THE PROCESS

FIELD OF THE INVENTION

The present invention relates generally to the field of steel mill dust treatment. More particularly, the invention comprises a hydrometallurgical separation process of dust produced by electric arc furnaces in steel mills. This process permits, on one hand, the decontamination of the dust and on the other hand, the production of ferrite and/or magnetite pigments useful in paints, plastics and concrete. The invention also comprises the pigments produced from this process.

PRIOR ART

Electric arc furnace (EAF) dust, also known under the name of (K061), is classified as a dangerous material because it contains high concentrations of soluble heavy metals such as cadmium, zinc, chromium and lead, but in particular lead. More specifically, EAF dust usually contains more than 5 ppm soluble lead and hence, does not meet the limits of lead specified by TCLP (Toxicity Characteristic Leading Prodecure). This dust also contains spinel compounds, notably magnetite (Fe_3O_4) and diverse ferrites $(MO_2Fe_2O_3)$. These spinel compounds as well as contaminants appear in the form of agglomerates and aggregates. To the naked eye, the dust is brown and an observer, even with the aid of a magnifying glass, will not notice the presence of black balls of magnetite, even if certain black balls can attain 150µm in diameter. The brown ferrite contained in the dust is ultrafine, and as a pigment, coats by adsorption the larger particles of magnetite.

Table 1 shows the typical chemical composition of EAF dust coming from two distinct steel mills. These compositions show elevated concentrations of certain heavy metals.

TABLE 1

CHEMICAL ANALYSES OF EAF DUST COMING FROM TWO DISTING STEEL MILLS IN THE PROVINCE OF QUEBEC

			SAMPLES	
Elements	Code	Units	MILL 1	MILL 2
AL	ICP90	ppm	7100	4500
Ba	ICP90	ppm	157	120
Ca	ICP90	ppm	107800	146000
Cd	ICP90	ppm	153	200
Co	ICP90	ppm	14	61
Cr	ICP90	ppm	1200	1400
Cu	ICP90	ppm	1720	1700
Fe	ICP95	ppm	>30	258000
K	ICP90	ppm	17700	7400
Mg	ICP90	ppm	49200	22200
Mn	ICP90	ppm	15300	27200
Mo	ICP90	ppm	18	41
Na	ICP95	ppm	33300	9700
Ni	ICP90	ppm	125	130
P	ICP90	ppm	500	670
Pb	ICP90	ppm	10950	9500
Si	ICP95	ppm	15500	15800
Ti	ICP90	ppm	700	600
V	ICP90	ppm	98	n.d.
Zn	ICP90	ppm	93900	162000

5   Most EAF dust treatment processes in the prior art aim at recovering or removing the heavy metals in an "aggressive" manner, attacking the cristallographic structure of the spinels.

Also known in the prior art, is EP 0 853 648 (equivalent to US 6,022,406), which describes a hydrometallurgical process of EAF dust treatment with the aim to

produce pigments. This process comprises a step of magnetic separation of the dust into two fractions, one fraction containing less magnetic elements, and the other fraction containing non magnetic elements, as well as treatment steps of these two fractions to obtain zinc ferrite pigments. The process disclosed also has

5   as an effect to attack the cristallographic structure of spinels other than the zinc ferrite spinel, and in this sense, is also an aggressive process.

Therefore, there is presently a need for a treatment process of EAF dust that permits an efficient and unagressive recuperation of the different ferrites and magnetites present in the dust, as well as permitting the decontamination of the

10   dust.

SUMMARY OF THE INVENTION

One objective of the invention is to propose a treatment process of EAF dust that responds to this need.

According to the present invention, that objective is accomplished with a

15   hydrometallurgical process for the treatment of steel mill electric arc furnace (EAF) dust containing agglomerates of small ferrite particles and larger magnetite particles, the ferrite particles coating by adsorption the larger magnetite particles, the dust further containing calcium oxide, zinc oxide and a toxic amount of leachable lead together with minor elements selected from the group consisting of

20   Mg, Cr, Cu, Cd, V, and chlorides. The process comprises the steps of:

a) washing the EAF dust in water to dissolve soluble salts, metals and simple oxides contained in the dust, the washing step being performed with an alkaline pH;

b) decanting the solution of step a) to obtain a supernatant liquid containing the

25   dissolved salts, metals and simple oxides, and a slurry containing ferrites and magnetites, a non toxic amount of leachable lead and a reduced amount of calcium;

4

c) separating the slurry and the supernatant liquid;

d) adding to the slurry obtained in step c) an anionic surfactant to disperse the ferrite particles adsorbed on the magnetite particles; and

e) treating the slurry from step d) to produce pigments selected from the group
5   consisting of ferrite pigments, magnetite pigments and ferrite/magnetite pigments.

Preferably, the sequence of steps a) to c) is performed more than one time before adding the anionic surfactant.

The use of an anionic surfactant was found to increase the efficiency and quality of further separation steps such as screening, and ferrite/magnetite separation by
10 a magnetic separator. Steps a) to c) also enable the decontamination of the dust by leaching salts, metals and simple oxides such as lead oxide. This selective solubilization is due to the alcaline pH solution, which is preferably greater than 12, resulting from the first washing, and optional second washing, with water. This alcalinity promotes the solubilization of PbO and, with the addition of surfactant,
15 enables the product to pass the test set out by the TCLP, which regulates standards of dangerous materials.

Advantageously, the process of the invention also enables the separation of the ferrites from the magnetites without breaking the cristallographic structure of the spinels, so as to produce magnetite and/or ferrite pigments of different grades,
20 whose different compositions have commercial values.

The process also permits the decontamination of EAF dust by hydrometallurgical means while maintaining the most stable families of spinels intact.

The solution obtained is step a) described above has a positive zeta potential, and the anionic surfactant is preferably added in a concentration sufficient to reduce
25 the zeta potential to or close to the isoelectric point, and more preferably to the isoelectric point.

The anionic surfactant is preferably a phosphate or an equivalent thereof. More preferably, sodium metaphosphate is used as the surfactant.

The use of sodium metaphosphate presents the following additional advantages to the process. Sodium metaphosphate converts the calcium and calcium
5   hydroxydes present in the liquid phase into a calcium phosphate which is precipitated with the solid. Therefore, this form of calcium sequestering allows for a quicker and sharper fractionation of the slurry by, for example, a drum magnet, and in addition when the slurry is eventually separated by screening, clogging of the mesh opening is minimized, and therefore requires less cleaning.

10   Step e) of treating the slurry preferably comprises the step of magnetically separating the slurry into a first fraction composed essentially of brownish ferrites and a second fraction composed essentially of black magnetite, the first fraction being less magnetic than the second fraction.

The magnetic separation is preferably performed with a magnetic field in the
15   range of 400 to 700 gauss, more preferably around 550 gauss.

In accordance with preferred aspects of the invention, the process further comprises steps of treating the first fraction to produce ferrite pigments and/or treating the second fraction to produce magnetite pigments.

Treatment of the first fraction (ferrite)

20   The step of treating the first fraction preferably comprises the steps of:

- removing from the first fraction, particles having a grain size of 20 μm or more, to obtain a refined first fraction;

- leaching the refined first fraction with a solvent, to obtain a leached slurry;

- separating the leached slurry into a solid fraction containing ferrite
25   pigments and a liquid fraction containing constituents of the first fraction soluble in the solvent; and

- drying the solid fraction to obtain dry pigments of ferrites.

In accordance with a first variant, the solvent is water and the ferrite pigments obtained are ferrite pigments of a first grade.

In accordance with a second variant, the solvent is sulphuric acid, the leaching is
5   performed at a pH of 0,5 to 3 and the ferrite pigments obtained are ferrite pigments of a second grade.

In accordance with a third variant, the solvent is nitric acid, the leaching is performed at a pH of up to 3, and the ferrite pigments obtained are ferrite pigments of a third grade.

10   In accordance with a fourth variant, the process further comprises the step of wet grinding the solid fraction to obtain a fourth grade of pigments having a finer mean grain size and a lower concentration of lead as compared to the ferrite of the third grade.

Treatment of the second fraction (magnetite)

15   The step of treating the second fraction preferably comprises the step of screening at 6 µm to obtain a first finer fraction with particles having a grain size of 6 µm or less, and a coarser fraction with particles having a grain size greater than 6 µm.

In that case, the process preferably further comprises the steps of: milling the
20   coarser fraction, and removing from the milled coarser fraction the particles having a grain size greater than 40 µm and returning these particles for further milling, and a second finer fraction having particles with a grain size of less than 6 µm, resulting in the coarser fraction containing particles having a grain size between 40 and 6 µm.

25   In accordance with a fifth variant of the process, the coarser fraction is preferably wet grinded by attrition to attain a mean grain size of approximately 0,3 µm.

The grinded product is thereafter filtered and dried to obtain a magnetite pigment of a first grade.

In accordance with a sixth variant, the first and second finer fractions, which contain particles of less than 6 µm, are purified by suspending residual contaminants contained therein with an anionic surfactant, to obtain a purified magnetic fraction. The purified fraction is thereafter decanted, wet grinded by attrition, filtered and dried, to obtain a magnetite pigment of a second grade.

Production of magnetite/ferrite particles

In accordance with a seventh variant of the invention, which does not involve magnetic separation, the process preferably comprises the steps of:

- removing from the slurry obtained in step d), particles having a grain size of 60 µm or less, to obtain a refined slurry;

- leaching the refined slurry in nitric acid at a pH of about 3, to obtain a leached slurry with no or a controlled amount of ZnO, which retards the setting of concrete;

- separating the leached slurry into a solid fraction containing a mixture of ferrite and magnetite pigments and a liquid fraction containing constituents soluble in nitric acid; and

- drying the solid fraction to obtain dry pigments containing a mixture of ferrite and magnetite.

The pigments obtained with this variant are suitable for use in concrete formulation for retarding the setting of concrete or for coloring the same.

All the seven variants described above also preferably comprise the steps of:

- coating the pigments with an inorganic and/or organic coating; and

- micronizing the coated pigments.

The present invention also concerns ferrite pigments and/or magnetite pigments or a mixture thereof, obtained by the processes described above. It also concerns a ferrite pigment from EAF dust, showing a resistance to leaching; and preferably showing a color thermal stability at temperatures of 300°C and higher.

5   Preferably, the ferrite pigment provides anticorrosion properties to metallic paint formulation.

The present invention also concerns the use of a ferrite pigment as described above for incorporation in anticorrosive paint formulation, plastic formulation or concrete formulation; and the use of a magnetite pigment as described above for
10   incorporation in a paint formulation, plastic formulation or toner formulation to provide magnetic properties.

BRIEF DESCRIPTION OF THE DRAWING

The characteristics of the present invention will be best understood by reading in
15   a broad manner the following description of a preferred embodiment for carrying out the invention, while referring to the annexed drawing in which:

Figure 1 is a flow chart of the process according to a first variant suitable for producing ferrite pigments of the first grade.

Figure 2 is a flow chart of the process according to a second variant suitable for
20   producing ferrite pigments of the second grade.

Figure 3 is a flow chart of the process according to a third variant suitable for producing ferrite pigments of the third grade.

Figure 4 is a flow chart of the process according to a fourth variant suitable for producing ferrite pigments of the fourth grade.

25   Figure 5 is a flow chart of the process showing a fifth and a sixth variant suitable for producing magnetite pigments of the first grade and the second grade.

Figure 6 is a flow chart of the process according to a seventh variant suitable for producing ferrite/magnetite pigments.

Figure 7 is a graph showing extraction values for calcium, chromium, zinc and lead versus time, and using a hydrofoil impeller.

5   Figure 8 is a series of graphs representing the variation of the zeta potential, ph and conductivity versus the concentration of sodium metaphosphate for a partly washed dust slurry.

Figure 9 is a graph showing extraction values for calcium, chromium, zinc and lead versus time, and using a high shear impeller.

10   Figures 10 to 13 are graphs showing the granulometric distribution of the first fraction (ferrite fraction) after one or two passes in the grinder

Figure 14 is a photo of ferrite pigments taken with an AFM microscope after wet grinding by attrition, showing the state of agglomeration and the fine size of the constituent ferrite fragments.

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DESCRIPTION OF PREFERRED PIGMENTS PRODUCED WITH THE PROCESS OF THE INVENTION

Four grades of ferrite pigments, two grades of magnetite pigments and one grade of ferrite/magnetite pigments were produced in the pilot run. The ferrite pigments
20   were produced according to the first, second, third and fourth variants of the process shown in figures 1 to 4; the magnetite pigments were produced according to the fifth and sixth variant of the process shown in figure 5, and the ferrite/magnetite pigments were produced according to the seventh variant of the process shown in figure 6.

25   All pigment grades have been obtained by a substantially similar treatment. The processes use the same physical manipulation techniques, but differ in the specific leaching step which gives the pigments their desired chemical and

surface characteristics. In many cases, specific coating also gives the pigments even greater specific properties for more particular markets.

The novelty of the process for all grades of pigment resides in an initial treatment of the EAF dust with water with the addition of an anionic surfactant. This

5   surfactant increases the efficiency and quality of the ferrite/magnetite separation by the magnetic separator. This initial treatment also enables the decontamination of the dust by leaching salts, metals and simple oxides such as lead oxide. This selective solubilization is due to the alcaline pH>12 solution resulting from the first washing (first mixing) and rinsing (second mixing) with water (Table 2). This

10   alcalinity promotes the solubilization of PbO and enables for the product to pass the test set out by the TCLP, which regulates standards of dangerous materials (Table 3).

TABLE 2

WATER ANALYSES

First Treatment

	Chemical Analyses				
	Zn ppm	Pb ppm	Cr ppm	Cd ppm	Ca ppm
S99# 28 1T H2O	1.36	170	0.75	0	770
S99# 28 1T H2O/ LV	1.56	41	0.95	0	340
B99# 79 1T H2O	3.21	71.7	15.74	0	206
B99# 79 1T H2O/ LV	2.00	65.4	1.93	0	492

5

TABLE 3

TCLP RESULTS

FM #	Grade	Analysis of leachate				
		pH	Pb ppm	Cr ppm	Cd ppm	Zn ppm
1076	Ferrite pigments of the first grade	8.5	0	0.32	0	0
1084	Ferrite pigments of the first grade	8.7	0	0	0	0.17
1104	Ferrite pigments of the first grade		2	0.20	2	240

Ferrite pigments

First grade (F1)

The ferrite pigment of the first grade was produced with the aid of a solution containing an optimal concentration of surfactant, the concentration being a
5   function of the isoelectric point of the dust to be treated, and with a leaching hereafter referred as to the second treatment) with water only.

The first grade ferrite pigment contained a high quantity of lead that cannot be easily leached under normal pH conditions. After ten months and many agitations in water, this pigment showed no leaching of heavy metals (Table 4) and is
10   comparable to pigments of the second and third grade described below. Heavy metals, with the exception of 8% zinc in the resistant form of zincite, wave present and stabilized in the structure of certain ferrites and spinels.

13

TABLE 4

<u>WATER LEACHATE ANALYSES OF 10 MONTHS</u>

FM#	1061	1082	1084	1133	1076
Grade	B-HS4	B-HS	B-PE	B-PE	S-PE
	Third grade	Second grade	First grade	First grade	First grade
Chemical Analysis					
Pb ppm	2.0	UDL	UDL	1.0	UDL
Cd ppm	0.1	0.3	UDL	UDL	0.10
Cr ppm	0.14	UDL	UDL	0.01	0.53
Zn ppm	3.53	0.06	0.1	UDL	0.04
Ca ppm	9.1	18.8	24.6	90.2	107.0
Fe ppm	15.01	0.14	UDL	UDL	0.19
Sedimentation (cm)	1.6	2.2	2.4	2.5	3.5
pH	7.60	7.79	12.03	12.41	12.45

The varied acid leaching steps of the process left solid ferrites of varied compositions and, as experience has taught, the ferrites rich in Ca were less stable to leachings than zinc ferrites or other ferrites representing complex oxides of Ca, Fe, Zn, Mn, Mg, Ni, Cr, etc. The resistant ferrites left after leaching, which made up the pigment, gave the pigment a high thermal stability and resistance to leaching, which are a function of the ionic stoichiometry and of the type and quality of the composite cristalline structures.

On the other hand, the ferrite pigments of the first grade demonstrated high resistance to corrosion as demonstrated in the salt spray (mist) tests, allowing coated metallic plates to resist corrosion for more than 1500 hours in a salt mist, which is equal or superior to all other pigments, including those of commercial quality used in the tests.

The first grade ferrite pigment owes its corrosion (salt mist) resistance to CaO, which is sacrificed as $Ca(OH)_2$ and/or to the resulting alcaline viscosity (soapy appearance) associated with $Ca(OH)_2$ and the pigment's elevated alcalinity.

Second grade (F2)

The ferrite pigment of the second grade was produced in the same way as the first grade, except that the second treatment was performed with sulphuric acid.

The preparation steps for the second grade pigments were identical to those used for the ferrite pigments of the first grade, the addition of the surfactant occurring after the first washing but before the magnetic separation. For the second grade pigments, leaching using sulphuric acid at a pH between 0,5 and 3 allowed for the preservation of a certain quantity of hydrated calcium sulphate, the solubilization of all the Zn in the form of zincite (ZnO) and the stabilization of lead as a solid sulphate. Using this treatment, the effluents rich in zinc sulphate, are a suitable form of compound to be directly recycled back into an electrolysis process, in order to recuperate the value of the zinc. The calcium sulphates generated by the

leaching are not harmful in anticorrosion paints. Calcium sulphate is frequently used as a filler with pigments used in paints and is often desirable as a pigmentary additive. This pigment did not require wet grinding by attrition, nor did it require a second magnetic separation and a second screening after acid

5   leaching. The pigment was filtered in order to obtain an allowable soluble salt concentration of 0.3g/l mg, and was then dried and micronized.

In consequence, the second grade of ferrite pigments allowed for the conservation of a fraction of calcium, the transformation of lead oxide into lead sulphate (which is very stable) and the solubilization of zinc oxide into zinc sulphate. These

10   characteristics of the second grade pigment make this pigment an excellent colorant as well as a corrosion resistant pigment.

Third grade (F3)

The ferrite pigment of the third grade was produced in the same way as the first grade, except that the second treatment was performed with nitric acid.

15   The leaching with nitric acid enabled the preferential removal of lead and other heavy metals due to the oxidizing property of the acid. The leaching was performed at a pH between 0 and 3, which permitted the elimination of certain families of ferrites, as a function of the pH, in order to minimize the total lead in the pigment and to give a pigment with a particular signature with regards to its

20   composition, structure and surface characteristics. As an example, between a pH of 3 and 1.5, the ferrites displayed a zeta surface potential that is positive, but this potential became negative at a pH < 1.5. This charge characteristic influenced the acceptable coatings and their associated mechanisms.

The different ferrites issuing from these leachings, showed high heat resistant

25   capabilities, which are very valued pigmentary properties. This leaching also minimized the difference between the pigment colours and enabled a delta of variation of about 0.5 for pigments of different dust deliveries (Table 5). The properties were equal or superior to the pigments currently recognized on the

16

industrial market. This grade of pigment showed enhanced resistance to corrosion depending on the coating used and also displayed a thermal stability as they preserve their colour tint at temperatures exceeding 300 to 400°C.

TABLE 5

5   **E VARIATION OF FERRITE HS4 PIGMENTS (THIRD GRADE) FROM MILL 1**

FM	COLOR			Delta E
#	L	a	b	
1317	27.13	2.27	7.38	0.2
1318	27.1	2.36	7.35	0.15
1319	26.81	2.34	7.15	0.21
1320	26.82	2.4	7.25	0.17

This thermal resistance is a requirement for plastics, powdered paint and ceramics.

Fourth grade (F4)

10   The ferrite pigment of the fourth grade was produced in the same way as the third grade, with the addition of a wet grinding step.

This pigment can be used in concrete as a cement additive that increases the fluidity and compression resistance of the concrete. This pigment had a finer granulometry than the third grade, ferrite pigment and the ferrite/magnetite

15   pigment.

The ferrite pigments of the first, second, third and fourth gradse have applications in anticorrosive paints. The third grade can be used in plastics and powder paints due to its thermal resistance. This pigment can also be used as a cement additive, thinning agent and additive in high performance concrete. The major difference

17

between the second and third grade ferrite pigments lies in their surface properties.

Magnetite pigments

First grade (M1)

5   The magnetite pigment of the first grade was produced by grinding with a ball mill the magnetic fraction issuing from the magnetic separation. The ground fraction was passed through a screening between 38 and 6 µm, and wet grinding by attrition in order to result in a median granulometry of about 0,3µm. The pigment was then filtered, coated with an organic coating, dried and micronized.

10   ### Second grade (M2)

The magnetite pigment of the second grade was obtained by screening the magnetic fraction, which had already undergone ball mill grinding, at 6µm. This fraction was purified by putting the silica, carbonate and residual ferrite contaminants into suspension, with the aid of an anionic dispersive surface active.

15   More particularly, this pigmentary grade of magnetite was obtained by screening at 6µm the magnetic fraction of the magnetic separation and the fractions less than 6µm coming from the screening of the rough magnetite after its ball mill grinding. This fraction, which contained a concentration of magnetite, was purified by putting the silica carbonate and ferrite residue contaminants into suspension

20   with the help of a surfactant. Two successive treatments of adding surfactant, followed by a decantation of the magnetite and separation of the suspension, were required to obtain an adequately black product which was subjected to wet grinding by attrition in order to attain a desired granulometry. The solid was finally filtered with an organic additive, dried and micronized. This step of purification is

25   similar to the first treatment of the dust. The ferrites and contaminants were put into suspension, and the magnetite was decanted.

A rough non pigmentary magnetite was also produced. It was obtained after attrition grinding the magnetic fraction coarser than 30µm. The attrition cleans the surface of the magnetite spheres by wearing out the white coating of calcium and silicate initially present. This step improves the black color of the spheres and

5   eliminates the magnetites which are less resistant to abrasion. The 70 and 30µm product can be used as a toner in photocopy processing. The commercial niche of this solid depends on its granulometry, morphology, resistance to friction and magnetic properties.

Ferrite/magnetite pigments (FM)

10   Ferrite/magnetite pigment suitable as a colorant for concrete was produced with nitric acid at a pH of 3 but without magnetic separation. The slurry from the first treatment was subjected to the following steps: screening at 6 µm, leaching in nitric acid, filtration in order to reduce its soluble salt content, and drying in a flash dryer, yielding a coarse pigment made up of agglomerates having a median grain

15   size of 5µm.

The screening enabled the removal of coarser contaminants including silica, coal and other fragments. After this, the slurry containing a magnetic charge underwent leaching with nitric acid at a pH of 3 in order to remove the zincite, since zincite delays the setting of cement. The product was filtered in order to

20   reduce its soluble salt content, after which drying in a flash dryer gave the pigment a granulometry with a median of about 5 µm.

For this grade of pigments, the initial pilot process was greatly simplified, which translates into a reduced production cost.

Because its granulometry is too large, the pigment cannot be used as an additive

25   in cement, in order to make high performance concrete.

For all grades of pigments, whether ferrite pigments, magnetite pigments or ferrite/magnetite pigments, at the end of the treatment, an organic additive was provided for the finished product in order to standardize the surface charges, to

19

facilitate the incorporation of the dry pigment into paint resins, and to give a desired fluidity for its handling. It is however worth mentioning that the coating step is optional to the process.

DESCRIPTION OF PREFERRED VARIANTS OF THE PROCESS ACCORDING TO THE INVENTION

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The process for treating EAF dust according to the invention is a hydrometallurgical process for the treatment of steel mill electric arc furnace (EAF) dust that contains agglomerates of small ferrite particles and larger magnetite particles, the ferrite particles coating by adsorption the larger magnetite particles,

10   the dust further containing calcium and toxic amount of leachable lead together with minor elements selected from the group consisting of Mg, Cr, Cu, Cd, V, and chlorides.

Ferrites represent a complex family of compounds represented chemically by the major elements Ca, Fe, Zn, Mg, which are the major and important elements in

15   this process together with minor elements selected from the group consisting of manganese, chromium, copper, cadmium, lead, vanadium and chlorides. Most of the elements are represented as oxides; either complex oxides like the ferrites or simple oxides represented by PbO, ZnO, CaO some other salts and metals are also present. This process also applies to EAF dust with low zinc content

20   generated from the use of pre-reduced iron ore pellets of hematite.

The process steps according to different preferred variants of the process are illustrated in figures 1 to 6, for the different grades of pigments. They show a hydrometallurgical batch process with no atmospheric emissions. The dust slurry of the first washing step is composed essentially of ferrites (65-75%), magnetites

25   (20-28%), zincite (ZnO) and litharge (PbO) (8%), CaO/Ca(OH)2 (5-12%) and variable concentrations of silica and coal.

One difference between the process of the invention and the prior art of EAF dust treatment processes, lies in the fact that the profitability of the present process is

not a function of the zinc concentration of the EAF dust. One of the steel mills that will be seen in an example uses an EAF feed of at least 50% pre-reduced hematite, with 50% scrap iron of different grades. Depending on the required production, the percentage of hematite and scrap iron can vary. For this steel mill, the dust's average zinc concentration is close to 9% compared to 16-22% for dust generated from feeds composed of scrap iron only. Table 1 shows two chemical analyses of EAF dust from the two steel mills in Quebec, that were used for testing the process.

The optimization and characterization of the test pilot run were effected by:

•   conducting physiochemical analyses: chemical analyses, granulometric distribution tests, and identification of chemical phases by X-ray diffraction and electronic microscopy, etc.;

•   optimizing the efficiency of the yield at different stations by measuring the volume and concentration (g/l) of the slurry, the weights of their solid fractions, and the processing time; the pH and electric conductivity of the liquids being also measured, etc.;

•   noting the pH and the electrical conductivity of the liquids;

•   evaluating the pigments by noting the colour specifications of the solid, humidity, oil absorption capacity, quality of dispersion, and salt mist tests, etc.

FIRST TREATMENT

The process comprises a first treatment which essentially consists of washing and rinsing the EAF dust for reducing the amount of calcium and soluble lead, to thereafter facilitate further treatment of the dust to produce commercial grade pigments.

More specifically, the first treatment, which is performed in a tank (10) comprises the steps of :

a) washing the EAF dust (12) in water to dissolve soluble salts, metals and simple oxides contained in the dust, the washing step being performed with an alkaline pH which is preferably greater than 12;

b) decanting the solution of step a) to obtain a supernatant liquid (14) containing

5   the dissolve salts, metals and simple oxides and a slurry (16) containing ferrites and magnetites, a non toxic amount of leachable lead and a reduced amount of calcium;

c) separating the slurry (16) and the supernatant liquid (14); and

d) adding to the slurry obtained in step c) an anionic surfactant (18), preferably a

10   phosphate and most preferably sodium metaphosphate, to disperse the ferrite particles adsorbed on the magnetite particles. It is worth mentioning that another anionic surfactant known in the art and that would have the same effect of dispersing the adsorbed ferrite particles is within the scope of the present invention.

15   Preferably, the sequence of steps a) to c) is performed more than one time before adding the anionic surfactant.   Note that steps a) to c) are not shown in the figures.

Steps a) to d) are performed in the tank (10) shown in each of figures 1 to 6. After the first treatment, the slurry (16) from step d) is sent to further stages of the

20   process to produce pigments selected from the group consisting of ferrite pigments, magnetite pigments and ferrite/magnetite pigments.

The treatment of the slurry (16) will vary depending on the grade of ferrite or magnetite to be produced. The production of each of these grades according to the process of the invention will be described in further detail further below.

25   **Example**

An example of the first treatment is now described in further detail.

Washing and first agitation

The EAF dust was washed with water under agitation provided by a hydrofoil impeller with a rotation speed of approximately 350 rpm in a tank. The height of the fluid level and the tank diameter had a ratio of 1:1. The tank agitation system

5   also comprised four baffles, which acted as static agitators.

The concentration of the slurry was 16%. Tests were made with batches of 10, 20 and 30 kg of dust for 60 liters of liquid, corresponding to solid concentrations of 16, 32 and 48% respectively..

The washing provided:

10   •   an aqueous solution of alkaline pH>12;

•   a dissolution of soluble salts, heavy metals and simple oxides under alkaline conditions (see Table 2) (this chemical charge was the liquid that is eliminated by decanting and pumping the supernatant liquid);

•   the initiation of the break-up of ferrite particles that are weakly linked

15   (Figure 7);

•   the dissolution of CaO and some calcium ferrites into soluble calcium and $CaOH_2$, and the dissociation of lead oxide;

•   the transformation of the CaO fraction abundant in $CaOH_2$ and the dissolution of lead oxide;

20   •   It is worth mentioning that greater agitation with other types of cutting agitators may unfavorably result in elevated concentrations in Ca and Pb in the liquid, which could hinder subsequent treatment steps.

•   The duration of agitation was 60 minutes and it was followed by a decantation period of 60 minutes and a separation of the supernatant liquid.

23

Given the high specific weights of the ferrites and magnetites, decantation of the slurry solid was used instead of filtration.

Rinsing and second agitation

The slurry from the washing was rinsed with water. Water is preferable:

5   •   to recuperate the metals and alkaline water of pH 12 from the interstitial water in the 20 liters of residual pulp of the first mixing; and

•   to continue the leaching of the calcium, lead and zinc in the dust.

The rinsing was carried out for a period of 60 minutes, followed by a 60 minute decantation and recuperation of the supernatant liquid.

10   Addition of surfactant

The addition of a surfactant had various objectives in the process. Firstly, it reduced the positive charge of the fine particles of the pulp represented by a zeta of 32 mV in order to attain the isoelectric point (zeta of 0 mV) for the system (slurry). This reduction of the charge of the chemical phases of the system

15   facilitated the fractionation of the composites. Further details on the effect of the surfactant on the charge of the chemical phases are given in the section entitled "Magnetic separation" hereinbelow. Secondly, when a phosphate such as sodium metaphosphate was used, the surfactant temporarily confined the CaO coming from the ferrites by coating the surface of the particles with phosphate. Also, the

20   surfactant was able to convert the calcium already in solution into calcium phosphate, which was insoluble in the solution and was concentrated with solid. It was also believed that some of the lead in solution is also precipitated in the form of a lead phosphate or in the form of a calcium and lead phosphate phase.

These deductions are supported by titration of the slurry with sodium

25   metaphosphate, which is the preferred surfactant (Figure 8). The conditions of the tests whose results are shown in Figure 8 were: 5% of solid in a slurry of 240ml; titration with the sodium metaphosphate of 3.6% (w/w) (22ml of the solution was

used); zeta potential calculated by using a laser volume median; S.G. 4g/cc. The graph showing Zeta vs. Surfactant Concentration, shows the reduction of the positive charge down to the isoelectric point. The graph showing Conductivity vs. Surfactant Concentration represents the concentration of ions in the supernatant

5   liquid, which decreases with the addition of surfactant.

After the addition of surfactant, agitation was resumed in order to standardize the state of the mixture and the feed of the magnetic separator which was fed at a flow rate of 1 l/min. The slurry was fed into the magnetic separator while agitating in such a way as to maintain the slurry homogenous in its magnetite and ferrite

10   content throughout the tank.

After the agitation step and the two decantation steps, the alkaline solutions of the effluents (80 liters) were used in the effluent treatment. The alkaline liquid was mixed with the acid effluents of the second treatment which will be described further below, in order to neutralize their acidity and to promote precipitation of the

15   metals in solution.

This first treatment (washing) of the raw EAF dust, which generated an alkaline solution, also promoted the solubilization of soluble salts in simple lead and zinc oxides to a concentration that satisfies the governing standards of the TCLP test, and the rules governing dangerous materials. In other words, the leachate of the

20   dust did not exceed the TCLP (Table 3) standard and thus is neither considered as contaminated, nor held under the rules of dangerous materials.

The role of agitation in the first treatment

Agitation tests were performed under variable times from 15 to 60 minutes, using a hydrofoil impeller. The resulting granulometry of the solid fraction of the slurry,

25   was obtained by a granulometer able to measure to the scale of a nanometer, according to the settings of number, surface and volume (Figure 7). The corresponding granulometric variation after 60 minutes indicated an acceptable size, with a median of roughly 0,6μm for the solid. This diameter was further reduced during the leaching of the second treatment. With other impellers, which

had higher shear levels, the resulting granulometry was too fine for optimizing the first treatment. Other agitation tests, in which the surpernatant liquid was analyzed after filtration for lead and calcium content, were performed and the results are presented in Table 6, and in Figure 9. The chemical concentrations resulting from

5   the test with the hydrofoil impeller indicated a stable concentration for an agitation time of 60 min. This agitation time represented a maximum for the extraction of calcium, and a plateau of saturation for the value of lead. For the other impellers, the elemental concentrations were too high, and thus not optimized.

26

TABLE 6

LEACHING OF EAF DUST DURING THE FIRST

TREATMENT AT VARYING TIMES

Run#1: 10kg on the
system of 1T of the
pilot plant;

Results of the AAS
Analysis

time	Pb	Ca	Cr	Zn	pH
min.	ppm	ppm	ppm	ppm	
0	22	0.6	39.71	4.88	
15	60	111.1	35.53	9.72	
30	72	166.1	33.3	6.48	
45	78	180	33.3	6	
60	78	190.3	27.17	9.18	
Washing					
15	77	323.4	5.31	3.7	12.67
30	77	352	4.92	3.74	12.69
45	88	226.6	4.5	4.18	12.71
60	88	172.7	4.81	4.36	12.72

After the first treatment which is performed in the tank (10) of figures 1 to 6, the slurry (16) is either sent to the magnetic separation (20) to separate the magnetite particles and the ferrite particles, as in figures 1 to 5, which show the first to sixth

5   variants; or it is sent to screening (30) and thereafter to the second treatment (40), as in figure 6 which shows the seventh variant, to ultimately produce a pigment of ferrite and magnetite suitable for use as a colorant for concrete.

The first to the sixth variants, which concern the production of ferrite pigments (figures 1 to 4) and the production of magnetite pigments (figure 5), will now be

10 described in further detail while referring to figures 1 to 5. For each of these variants, as broadly described, the slurry (16) from the first treatment was subjected to a magnetic separation (20) to obtain a ferrite fraction (24) and a magnetite fraction (26). Both these fractions (24 and 26) were respectively subjected to a screening (30 or 32).

15 Referring to figures 1 to 4, the refined ferrite fraction (34) from the screener (30) was further subjected to a second treatment (40) depending on the grade of ferrite pigments produced. In the case of the third and fourth variants (figs 3 and 4), the second treatment was preceded by at least one of the following steps: decantation (60), grinding (50 or 55), and magnetic separation (200). After the second

20 treatment (40), the slurry (46) obtained was subjected to filtration (70), and thereafter to the typical process steps used in the field of pigment production, as for example drying (90), coating (80) and micronization (100).

The filtration step (70) produces water to be recycled (72).

It is also worth mentioning that in the first and the third process variants, the

25 second treatment was preferably followed by a second magnetic separation (200, 220) used to separate the magnetite fraction (202, 222) that remained in the slurry (46) from the ferrite fraction (206, 226). The ferrite fraction (206, 226) was sent

back to the ferrite production line for producing the ferrite pigments, whereas the magnetite fraction (202, 222) was sent to the magnetite production line.

5   Referring to figure 5, the magnetic fraction (26) from the magnetic separation (20) was sent, preferably with magnetic particles (202, 212, 222) from other steps of the process, to a first screening (30) at 150 μm. The fraction (38) of less than 150 μm was sent to a ball mill (500) and then to a second screening (32) to obtain a first finer fraction (304) with particles having a grain size of 6 μm or less; and a coarser fraction (306) with particles having a grain size greater than 6 μm. The

10   coarser fraction (306) was then milled and screened at 40 μm (these steps are not shown on figure 5) to finally obtain a coarser fraction containing particles having a grain size between 40 and 6 μm.

15   The coarser fraction (306) was wet grinded by attrition (50) to attain a mean grain size of approximately 0,3 μm. It was thereafter subjected to the typical process steps used in the field of pigment production, as for example drying (90), coating (80) and micronization (100).

20   The finer fractions (304) were purified by suspending (600) residual contaminants contained therein with an anionic surfactant (802), to obtain a purified magnetic fraction (602).

MAGNETIC SEPARATION (20)

25   The magnetic separation step (20) yields the first fraction (24) containing in a major portion ferrite particles and the second fraction (26) containing in a major portion magnetite particles.

In the raw EAF dust, the black magnetite is never apparent or visible to the naked eye, even though the magnetite is large and rough compared to the other

components of the dust. This phenomenon is explained by the adsorption of the ferrites to the surface of the magnetites. In the raw dust, the ferrites are positive and the magnetite is negative, which causes an electrostatic attraction between these two chemical phases. This charge can be measured with an apparatus

5   called " Electroacoustic Sonic Amplitude (ESA)", which enables the calculation of the zeta potential of the particles in aqueous medium, and the indirect and qualitative evaluation of the surface charge of the particles. The results indicate that ferrites have a positive charge with a zeta of +27 mV, whereas the magnetites are lightly negative and have a zeta of –3 mV, which corresponds to the charge

10   values for naturally occurring magnetites. Also, given that the ferrites have a granulometry under 1 μm, they will coat the large rough surface of the magnetite. This rough texture of the magnetite surfaces seems to be produced by the deposition of phases of calcium and other composites which can be removed by attrition. These factors render it difficult to separate ferrites from magnetites.

15   Laboratory experience teaches us that without a surfactant, it is possible to obtain a fraction concentrated in magnetite, but this fraction is brown and not black, and has a large proportion of ferrites trapped with the concentrated magnetite.

In the process according to the invention, by adding an anionic surfactant (preferably sodium metaphosphate), the positive charge of the ferrites is

20   neutralized and can be inverted to attain negative charges with an intensity of –40 to -160 mV, and lower. The addition of surfactant increases the surface charges of the fine ferrites, decreases the cohesion or the attraction between the ferrites and magnetites, causes a stronger repulsion between the particles of ferrites and maintains these ferrites in suspension. The coarse magnetic fraction, which has a

25   very small specific surface, is not greatly affected by the addition of surfactant. The granulometry and the mass of the magnetites enable the decantation of the magnetite with the ferrite in suspension. This procedure substantially improves the results of the magnetic separation and the screening. The condition at the isoelectric point is preferable in order to optimize the magnetic separation and the

30   screening (see next section), while controlling the concentration of lead in the solid.

Evaluation of the results

Magnetic separation in aqueous medium was performed with a drum for which a magnetic field was generated by an electro-magnet with a maximum power of about 1200 gauss. The slurry (16), which had a concentration of solids of 16%

5 and a mass concentration of surfactant varying from 0,1% to 1,3%, was used in the separation. Magnetic separators are well known and do not need further description. The slurry (16) was fed with a flow rate of 1 l/min. To unstick the magnetic fraction from the drum, an additional flow of water (22) of 1,4 l/min was added, totaling 150 liters of liquid (to recycle) with a concentration of 3% solids to

10 be recuperated by decantation (60) and screening (30).

The maximum fraction of magnetite recuperated in the pulp varied from one company to another according to its production. However, the maximum fraction recuperated was on the order of 15 to 20% for the producer using a pre-reduced hematite mineral and between 8 to 10% for the producer using scrap iron only.

15 The quality of separation was qualitatively evaluated under the microscope by observing the colour, which distinguishes magnetite from coal. Colour is also used to evaluate the quality of magnetic separation. Table 7 compares the three components of colour, according to the HunterLab color scale, for the raw dust for separation, and for the separated and screened fractions of ferrites and

20 magnetites. The parameter "L" of 0,00 corresponds to a black standard used to calibrate the apparatus whereas the value 100,00 is associated with the white standard. The parameter "L" indicated a paler shade for the fractions obtained without the addition of surface active, and which, in consequence, only contained a concentration of magnetite still coated with brown ferrites. On the contrary, with

25 the addition of surface active, the magnetic fraction was of a blacker shade according to the optical apparatus and also according to the naked eye.

TABLE 7

COLOR COMPARISON FOR THE EAF DUST, FERRITE AND MAGNETITE, SEPARATED BY MAGNETIC SEPARATION (MSP)

Samples	Color		
	L	a	b
Raw Dust from mill 2	29.09	2.52	8.60
Sample before MS with 0.4% NaMP	28.63	2.05	8.01
Sample after 20 µm Screening	28.30	1.75	7.67
Sample of Raw Magnetite < 38 µm	25.73	-0.23	3.08

5   The efficiency of the magnetic separation is supported by the mass values of the quantity of ferrite trapped by the magnetite. The weights of the fractions indicate that without the addition of surfactant, the ferrite trapped by the magnetite reached a maximum. On the other hand, with the addition of a surfactant, the quantity of ferrite decreased (Table 8). The adsorption of the surfactant occurred

10   preferentially on the fine fraction of the solid and thus in this case, on the ferrites. The magnetites, being rougher, experienced a change in charge that is less significant and thus there less of an effect on the mobility of this phase.

32

TABLE 8

QUANTITY OF FERRITES TRAPPED BY MAGNETITE

AS A FUNCTION OF SURFACE ACTIVE

Tank	Base	NaMP	MS < 6 µm g.	Average weight g.	Difference with v. without NaMP in g. ou %
B99# 143	MP-060/ISP	without	1933	1961	
B99# 144		without	1990		
					142 g. or 7.2%
B99# 145		with	1849	1819	
B99# 146		with	1790		
S99# 71	MP-060-070-120/STE	without	712		
					45 g. or 6,3%
B99# 68	MP-060-070-120/STE	with	667		

Another indication of the efficiency of the separation is provided by the results of
the tests of recuperation of magnetite obtained from the rough fraction $\geq 20\mu m$
after screening the non magnetic fraction. This ferrite fraction comprised rough
contaminants (i.e. coal) and magnetite, with a smaller amount of fine silica and

5   carbonates or calcium phases. The magnetite was not separated in the first
magnetic separation as it was coated with silica and phases of calcium. The
trapped quantity varied with the quantity and concentration of the added
surfactant. For a separation without surface active, 197 g of rough magnetite was
recovered. The same fraction after having added the surface active resulted in a

10   recuperation of 221 g, or 11% more magnetite recovered. This result is explained
by the fact that the surface active is more efficient in dispersing fine particles, and
thus the finer contaminants from the larger spheroids of magnetite; coal does not
influence the separation.

For the process according to the invention, it is preferable to use the surfactant

15   according to a specific dosage in order to produce two fractions (24 and 26) that
are adequate for realizing products suitable for commercial applications, as will be
explained in more details further below.

SCREENING (30 or 32)

Screening of the ferrite fraction (24) or the magnetic fraction (26) is essential to

20   produce ferrite pigments or magnetic pigments having a commercial value,
because it allows the physical separation of larger agglomerates and certain
contaminants accompanying the ferrites and magnetites. All particles or
agglomerated substances of more than $20\mu m$ with or without magnetic
susceptibility, can be separated. Coal and even partially fused scrap metal

25   fragments are separated by screening.

In addition to improving the separation of the ferrites and magnetites in the first
treatment and the magnetic separation, the addition of surfactant prevents the
clogging of the screens and enables screening with openings of 20 to 6 µm. The
clogging is caused by portlandite, a calcium hydroxide $Ca(OH)_2$, which is

produced from lime in the raw EAF dust. Portlandite in solution and in suspension is deposited on the walls of containers and, in particular, on the mesh of the screens, thus sealing the latter. By using an appropriate surface active (sodium metaphosphate), the calcium in solution is precipitated in the form of calcium

5   phosphate. This precipitation is associated with the decrease in conductivity observed during the addition of surfactant and this decrease continues after reaching the isoelectric point, attaining, in certain cases, a minimum of conductivity (Figure 9).

The screening tests demonstrated that the more the surface active concentration

10   is increased, the more the solution approaches a minimum of conductivity and the less clogging of the screens is observed. Also, the inner walls of the tanks, screens and other equipment can be easily cleaned by simply rinsing with water.

If no addition of a surfactant is used, the portlandite which adheres to surfaces and screen mesh, must be cleaned with an acidic aqueous solution. The

15   concentration of surfactant giving the minimum of conductivity is not preferred because such a high concentration of sodium metaphosphate interferes with the leaching of lead in the pulp.

The addition of surface active to give the isoelectric point was sufficient to double the slurry flow rate into the screens from 4 l/min to 7 or 8 l/min and thus increase

20   the capacity of filtration. The addition of surface active decreased the number of required cleanings for a tank of 10 kg using a screen of 20 µm by a factor of three.

In addition to the slurry, a flow of water for screening (32) is used to facilitate the screening.

In the first to third variants, the rough screened fraction (36) issued from the first

25   screening (30) was subjected to a magnetite separation (210) used to separate the magnetite fraction (212) that remained in the ferrite fraction (24). The magnetite fraction (212) was sent to the magnetite production line, as shown in figure 5.

WET GRINDING or grinding by attrition (50)

This wet grinding can be accomplished with silica sand, zirconium balls or other materials with a spherical morphology and sufficient hardness to resist abrasion. The results provided were obtained with the zirconium beads with a range of
5   granulometry of 0,4 to 0,6 mm in a horizontal grinder, with horizontal type disks. The grinding conditions and results are presented in Table 9.

TABLE 9

WET GRINDING CONDITIONS AND RESULTS FOR FERRITES

1. Wet Grinding Conditions for Ferrites

	Feed flow rate	Pulp conc.*	Disk speed	Amperage	Media	Load
Condition #1-2	0,2 l/min	350 g/l	27k FPM	3.8	Zr/Sr 0,4-0,6mm	80%
Condition #1-4	0,5 l/min	350 g/l	27k FPM	3.7	Zr/Sr 0,4-0,6mm	80%

2. Wet Grinding Results for Ferrites

	Surface area	Volume	Viscocity
	micron (APS)	micron (APS)	cps
Condition #1-2	0.276	0.432	810
Condition #1-4	0.252	0.517	470
pulp before grinding	0.415	6.307	124

* The pulp used in the optimization tests is a B99

The goal of this grinding is to break the large aggregates of more than 5 to 20 µm in order to give the ferrite pigment particles a restricted range of granulometry, more specifically, a bell curve distribution with a median around 0,3 µm. The granulometric distribution after wet grinding assures that the fraction of rough aggregates of the dust is eliminated and transferred into the range of fine granulometry. The obtained diameter (in surface) is from 0,25 to 0,28 µm, with a bell curve distribution desired for the pigments. The results are illustrated in figures 10, 11, 12 and 13. Figures 11 and 12 illustrate the granulometric distributions for slurries after one and two passes in the grinder. For more aggressive leaching processes, as for the second grade ferrite pigment, the slurry does not require grinding, the granulometric median being already close to or just under 0,8 µm. Normally, the first grade ferrite pigment requires grinding in order to obtain an adequate dispersion. Also, some dusts may contain enough aggregates around 20µm as to require the use of a wet grinder. For cement additives, wet grinding is necessary, because it decreases the granulometry, increases the surface contact between the particles, and generates new surfaces for a more efficient leaching at the second treatment (40).

The ferrite pigment particles, even after grinding, are still aggregates of fine nanometric particles. Figure 14 (AFM microscope) confirms this state of agglomeration and the fine size of the constituent beads or fragments.

SECOND TREATMENT (40) OF THE FERRITE FRACTION

The goal of the second treatment (40) is to leach the heavy metals still in the slurry, to eliminate the less stable ferrites and give certain required surface characteristics to the pigments (sign and zeta potential intensity), in order to improve the pigment compatibility in paints, plastics and concrete.

The chemical composition of the pigmentary spinels resulting from the second treatment (40) is represented by the chemical compositions given in Table 10.

These pigments represent various slightly differing ferrites or spinels rich in iron, zinc, magnesium and manganese and contain the elements Al, Si, Pb, Ni, Cr etc, as minority components. All minority components are stabilized in the structure of the spinels and the lead adheres to the leachate criteria of the TCLP and to the

5   norms and expectations used by paint manufacturers of which the most stringent imposes a maximum concentration of 500 ppm of lead in paint.

39

TABLE 10

VARIATION OF CHEMICAL COMPOSITION OF THE

PIGMENTS FERRITE IN FUNCTION OF pH

			SAMPLES			
Elements	Code	Units	Fm# 1226	Fm# 1217	Fm# 1314	Fm# 1491
			pH 3,0	pH 2,0	pH 1,5	pH 0,5
AL	ICP90	ppm	4500	4000	4100	3400
Ba	ICP90	ppm	70	51	45	n.d.
C	CHM118	ppm	3700	3700	n.d.	n.d.
Ca	ICP90	ppm	8800	5900	7200	6700
Cd	ICP90	ppm	107	101	112	90
Co	ICP90	ppm	11	<10	47	n.d.
Cr	ICP90	ppm	1580	1710	1920	1745
Cu	ICP90	ppm	2560	2510	2600	2645
Fe	ICP95	ppm	>30	>30	>30	528100
K	ICP90	ppm	600	400	500	n.d.
Mg	ICP90	ppm	24600	26800	28700	30100
Mn	ICP90	ppm	24450	27090	28260	25900
Mo	ICP90	ppm	<10	<10	11	n.d.
Na	ICP95	ppm	2700	2700	n.d.	n.d.
Ni	ICP90	ppm	187	187	219	n.d.
P	ICP90	ppm	11400	400	600	n.d.
Pb	ICP90	ppm	10870	3780	3030	1685
S	CHM12	ppm	100	100	n.d.	n.d.
Si	ICP95	ppm	12900	8800	n.d.	n.d.
Ti	ICP90	ppm	600	600	600	n.d.
V	ICP90	ppm	108	110	102	n.d.
Zn	ICP90	ppm	89140	91470	117300	100600

As an example, the effect of the second treatment is illustrated in Table 10 by the variation of lead for the different third grade pigment leached at different pHs with nitric acid. The most important variations are the lead concentrations and the zeta for the different pigments. The sign of the relative charge represented by the zeta

5   potential in aqueous medium is particularly important, the latter changing from +40mV for the first grade to –9 to 11 mV for the leached pigment at a pH of 1,5 to 0,5. This parameter is important for the behavior of the pigment and also influences the pigmentary properties and the coating mechanism, or even the type of coating it can accept, if required.

10   Conditions for the second treatment (40)

A pulp of 8 to 10% solids in 55 liters of water was acidified with nitric acid 6 N to the desired pH by continuous addition of acid for a period of 30 min. The pH was maintained for 60 min. by sporadically adding the acid while agitating the pulp. Decantation was preferred and the surpernatant liquid was removed.

15   In the first variant, simply water is used as the leaching agent. In the second variant, sulfuric acid (42) is used, and in the third variant, nitric acid (43) is used as the leaching agent.

PRODUCTION OF FERRITE/MAGNETITE PIGMENTS (SEVENTH VARIANT)

Referring to figure 6, and in accordance with the seventh variant used to produce
20   ferrite/magnetite pigment, the slurry (16) from the first treatment (10) was not subjected to magnetite separation. The slurry was rather subjected to a screening at the 60 µm or less. The finer fraction, hereinafter referred as to the refined slurry (33) was subjected to the second leaching treatment (40) with nitric acid (43) at a pH of about 3, to obtain a leached slurry (48) with no or a controlled amount of
25   ZnO which retards the setting of concrete. The leached slurry (48) was separated into a solid fraction (74) containing a mixture of ferrite and magnetite pigments and a liquid fraction (72) containing constituents soluble in nitric acid. The solid

fraction (74) was then dried (90) to obtain dry pigments containing a mixture of ferrite and magnetite.

SPECIFIC CHARACTERISTICS OF THE FERRITE PIGMENT OF THE THIRD GRADE

The pigmentary properties for the ferrite pigments of the third grade are shown in Table 11 along with the commercial pigments recognized as ferrites. These commercial ferrites are obtained by mixing oxides according to a company-specific formulation and then calcining at high temperature. The table shows different important quantitative pigmentary properties such as:

- pH;
- humidity;
- "long oil" absorption ;
- dry colour of pigment;
- paint colour;
- gloss;
- dispersion on the Hegman gage;
- resin incorporation time

TABLE 11

PIGMENTARY PROPERTIES OF FERRITE PIGMENTS

FM #	1000	1017	1323	1275	1224
Grade	Brun 10	130BM	B-HS4 (third grade) pH 1.5 0.3% NaMP	B-HS (second grade) pH 1.0	B-PE (first grade)
Note:	Shepherd	Bayer	with Wet Grinding (WG)		MS with surfactant WG normal
Dispersion:	STM1/020	STM1/020	STM1/020	STM1/020	STM1/020
	1 ¼	1 ¾	45 sec.	40 sec.	
	-	6 - 5½ LN 0	-		6 ½
	6 ½ - 7 N 5 ¼	Full Nibs	6 ¾ N 5 ½	6 ½ N 5	5 ¾ N 4

TABLE 11

PIGMENTARY PROPERTIES OF FERRITE PIGMENTS

Finished Paint:	10%	20%	10%	20%	10%	20%	10%	20%	10%	20%
		15.63		22.47	13.74	14.71	13.20	13.74	15.17	15.47
		8.76		25.04	3.29	3.00	3.30	3.21	3.37	3.20
		7.22		12.21	5.53	5.16	5.47	5.25	6.43	6.25
		80.6		47.3	75.3	73.4	69.4	63.7	82.0	86.2
		93.3		81.1	23.2	22.2				
					99.0	98.2	100.0	100.0	100.0	100.0
					1.89	2.15	1.74	1.89	2.30	2.39
					1.91	2.19	1.73	1.89	2.29	2.39
Pigmentary Properties:										
pH	8.9		7.4		6.3		5.7		11.7	
Humidity	0.17		0.26		0.75		0.45		1.47	

44

TABLE 11

PIGMENTARY PROPERTIES OF FERRITE PIGMENTS

Oil absorption	9.2	18.5	12.0	12.0	20.3
Soluble salts	0.12	0.14		0.23	0.41
325 mesh residu	0.022	0.853	0.039	0.059	0.098
Bulk Density				0.83 / 1.20	0.43 / 0.64
Dry color:	27.56 / 9.04 / 7.95	31.80 / 25.41 / 12.13	27.07 / 2.65 / 8.03	24.61 / 2.83 / 7.40	29.70 / 2.20 / 8.05
MP					
Humidity					

Another advantage of ferrite pigment of the third grade is its colour stability at temperatures exceeding 300°C. Table 12 shows the colour parameters for a ferrite before and after heating to 300°C.

5

46

TABLE 12

COLOR PARAMETER CORRECTION FOR HS4 FERRITE

PIGMENT (THIRD GRADE) BEFORE AND AFTER HEATING TO 300°C FOR 60 MIN.

FM#	Grade	Temp. °C	Time min.	Color	
				L	a
1257	B99-HS4 (third grade) pH 1.50	300	0	26.37	1.88
			60	26.82	2.53

Salt mist tests for the pigments for which the properties were presented in the preceding section, are given in Table 13 for exposure times of 500, 1000 and 1500 hours, in a chamber designed for accelerated corrosion testing.

48

TABLE 13

SALT MIST ACCELERATED CORROSION TESTS FOR FERRITES

Performance of coatings after 1512h

Coating Systems / Products	Corrosion ASTM D1654 /10	Formation of blisters ASTM D714	Swelling ASTM D1654	DIC* Peeling ASTM D1654 /10	DIC* Larg. Max. mm	Groove Zone Surface rust ASTM D610 /10	Groove Zone Formation of blisters ASTM D714 /10	Remarks
FM#1000-2 B-PE (first grade)	7.5	7G, 8M 1P	8	8.5	4	10	0	56.6 visual: 7
FM#1017-3 B-PE (first grade)	7.5	4G, 1M 6P	8.5	8.5	10	10	0	63.4 visual: 6
FM#1174-4 B-PE (first grade)	8	0G, 3M 0P	8	7.5	6	10	0	59.2 visual: 3
FM#1267-1 Zinc chromate	8.5	0G, 1M 1P	8.5	9	5	10	0	62.2 visual : 2
FM#1276-4	8.5	0G, 0M	8.5	9.5	3	10	0	40.2 visual : 1

5

49

Strontium chromate								
FM#1341-3	8.5	1P	8.5	8.5	10	10	0	54.4 — visual : 4
S-HS4 (third grade) pH 1,5		1G, 1M 2P						
FM#1364-1	8	1G, 5M 1P	8	8	9	10	0	53.3 — visual : 5
S-HS4 (third grade) pH 0,5								
Acceptable code	7 à 10		7 à 10	6 à 10	10	8 à 10		

*DIC : Corrosion induced loss of adherence
**ND : Not determinable

	Position 1512 h
FM# 1000 Brun 10 of Shepherd	6
FM# 1017 130 MB of Bayferrox	7
FM# 1174 B-PE	3
FM# 1267 Basic Zinc Chromate 233	2
FM# 1276 Strontium Chromate 177	1
FM# 1341 S-HS4 pH 1.5 (0,3% NaMP in granules)	4
FM# 1364 S-HS4 pH 0.5 (0,3% Na MP)	5
	17

SPECIFIC CHARACTERISTICS OF THE MAGNETITE PIGMENTS

Magnetite production uses the same treatment units with the exception of an impact grinder and a 6 μm screen. Normally, magnetite does not require leaching

5   with acid and its surface characteristics are more constant.

Two magnetites undergo wet grinding: (1) the magnetite fraction after impact grinding, between 38 and 6 μm and (2) the fraction of ≤6μm after the purification with the surfactants. In both cases, the particles are too coarse or large in diameter to be classified as pigments and require attrition. Zirconium beads of 0,4

10   to 0,6 or 0,8 mm were used to attain a median particle size of 0,3 μm. The initial concentration of the pulp was 350 g/l and the grinding was performed continuously until the desired granulometry was obtained.

The magnetite requires purification by putting ferrites and other contaminants such as calcium and silica into suspension. This suspension is accomplished with

15   the aid of an anionic surfactant such as sodium metaphosphate or saratan. The required dosage, in order to optimize the suspension, is obtained after titrating the pulp with the surfactant.

The results for the magnetite pigmentary properties of the present invention and the competitors' pigment properties are shown in Table 14.

51

TABLE 14

PIGMENTARY PROPERTIES OF MAGNETITE PIGMENTS

FM #		1335	1336	1239	1280	
Grade		B-Mag-PE (M1)	B-Mag-HS4 (M2)	Shepherd Black 376	Bayferrox 303T	
Note:		WG: SM 1.5/ 2h	WG: SM 1.5/ 2h	Magnetite		
Dispers ion:						
	Formula used:	SPTM1/0 20	SPTM1/02 0	SPTM1/02 0	SPTM1/02 0	
	Incorpor ation (min.)	21	15	40 sec.	30 sec.	
	Hegman: (N.S.) from 0-8	N 3	N 1	6 ¾ N 4 ½		
	from 4-8				8	

TABLE 14

PIGMENTARY PROPERTIES OF MAGNETITE PIGMENTS

FM #	1335	1336	1239	1280
Grade	B-Mag-PE (M1)	B-Mag-HS4 (M2)	Shepherd Black 376	Bayferrox 303T
Note:	WG: SM 1.5/ 2h	WG: SM 1.5/ 2h	Magnetite	
Dispersion:				
Formula used:	SPTM1/0 20	SPTM1/02 0	SPTM1/02 0	SPTM1/02 0
Incorporation (min.)	21	15	40 sec.	30 sec.
Hegman: (N.S.) from 0-8			6 ¾	
from 4-8	N 3	N 1	N 4 ½	8

TABLE 14

PIGMENTARY PROPERTIES OF MAGNETITE PIGMENTS

Oil absorption	(%)	23.1	21.3	12.0	14.8
Soluble salts	(%)	0.14	0.13	0.15	0.23
325 mesh residu	(%)	0.059	0.024	0.007	0.0194
Bulk Density	non-compacted	0.38	0.43	0.69	0.94
	compacted	0.63	0.71	1.24	1.33
Dry color:	L a b	24.55 0.07 3.86	23.61 -0.10 3.99	18.41 -1.03 1.00	19.71 -0.99 0.21
MP	L a b				
Humidity	(%)				

54

The salt mist tests are also represented in this table for the magnetites.

Magnetite has morphologic and magnetic properties that enable it to be used in inks (Toner) of photocopiers.

5   Although preferred embodiments for carrying out the invention were described in detail above and illustrated in the annexed drawing, the invention is not limited to these preferred embodiments, and many changes and modifications can be made by a person skilled in the art, without leaving the framework or the spirit of the invention.